2942 *Organometallics* 1989, *8*, 2942–2947

Synthesis of Group 6 Metalla-(Aza)-Crown Ether Tetracarbonyl Complexes with Potentially Anionic Amido Groups. The Influence of Li^+, Mg^{2+}, and Al^{3+} Cations on the Susceptibility of the Carbonyl Ligand to Nucleophilic Addition of Alkyl/Aryl Carbanions and Hydride

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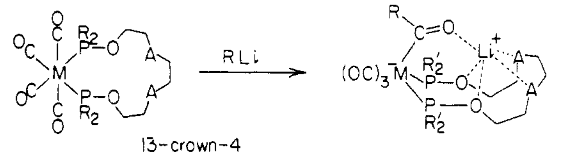
Received November 3, 1988

The reaction of $Mo(CO)_4$(norbornadiene) with the appropriate α,ω-di-P-donor ligands, containing amido functional groups using high dilution techniques, gives *cis*-$Mo(CO)_4P_2\supset$ complexes in 30–60% yields {where $P_2\supset$ = $R_2PO(CH_2)_3NHC(O)CH_2CH(Me)OPR_2$ [R_2 = Ph_2, complex **3**; R_2 = $MeNCH_2CH_2NMe$, **4**], $Ph_2PO(CH_2)_2O(CH_2)_2NHC(O)CH_2CH(Me)OPPh_2$ (**5**), $Ph_2PNH(CH_2)_3NMe(CH_2)_3NHPPh_2$ (**6**), $Ph_2PNHCH_2(CH_2OCH_2)_2CH_2NHPPh_2$ (**7**)}. Deprotonation of the amido NH(s) of these complexes lead to anionic 12C3, 13C4, and 14C4 metalla-aza-crown ether tetracarbonyls. Reaction of **3**, **4**, and **5** with PhMgCl leads to deprotonation of the amido group with no encapsulation of "Mg^{2+}" by the resultant anionic 12C3 and 14C4 ring systems. Reaction with RLi (R = Ph, Me) leads to an equilibrium mixture of (i) the deprotonated species, (ii) a species in which the Li^+ is partly encapsulated by the anionic amidate-crown ether ring (N^- and 2P*O* coordination to Li^+), and (iii) a benzoylate/acylate complex *fac*-$Mo(CO)_3(RCOLi)P_2\supset$ in which the Li^+ is completely encapsulated by the dianionic molybdenum complex. Addition of excess RLi forces the system to 100% benzoylate/acylate (IR monitoring, ν(CO) region). Complexes **6** and **7** and the non-crown ether system *cis*-$Mo(CO)_4\{Ph_2PNH(CH_2)_5NHPPh_2\}$ (**27**) react with 3 equiv of RLi to give *fac*-$[Mo(CO)_3(RCOLi)P_2\supset]Li_2$ which contains one Li^+ encapsulated by the trianionic complex. Reaction of these complexes with anhydrous $AlBr_3$ leads to neutral, isolable, and chemically relatively stable compounds *fac*-$[Mo(CO)_3(RCOAl)\{P_2\supset\text{-}2H^+\}]$. The stability of these benzoylate/acylate compounds, via â vis "$M(CO)_4(PR_3)_2$ + RLi systems" (no reaction), can be ascribed to preferential Li^+ or Al^{3+} binding by the product molecule. The reaction of **6** with 3 equiv of $LiAlH_4$ in THF solution resulted in the evolution of 2 equiv of H_2 gas, and the formation of a "*fac*-$Mo(CO)_3$" solution species tentatively formulated as the formylate $[Mo(CO)_3(HCOLi)P_2\supset]Li_2$ on the basis of IR [ν(CO)] and $^{13}C\{^1H\}$ NMR data. Similar reactions were observed when $3LiAlH_4$ was added to **7** and **27**. In contrast the molybdenum–crown ether tetracarbonyl *cis*-$Mo(CO)_4\{Ph_2POCH_2(CH_2OCH_2)_2CH_2OPPh_2\}$ does not react with $LiAlH_4$ under similar conditions.

Introduction

We have previously reported the synthesis of a range of group 6 metalla-crown ether tetracarbonyl complexes $M(CO)_4P_2\supset$ (e.g. **1**; M = Cr, Mo, W).[1-5] Studies showed that the 12C3 and 13C4 complexes were particularly suitable for the complexation of Li^+ cations in the benzoylate/acylate complexes $M(CO)_3(RCOLi)P_2\supset$ (e.g. **2**) formed from the reaction of $M(CO)_4P_2\supset$ with RLi (R = Ph, Me) (eq 1). The additional stability provided by preferential Li^+ binding by the benzoylate product, vis â vis $M(CO)_4(PR_3)_2$ systems with no crown ether potential (do not react with RLi), was estimated to be as much as 9–11 kcal·mol^{-1} and is particularly sensitive to the relative basicity of the P–O oxygens.[4,5] Attempts to obtain Na^+ analogues of **2** from the reaction of 16C5 and 19C6 metalla-crown ether tetracarbonyls with NaPh were not successful. Nor did the 12C3 and 13C4 systems react with RMgCl reagents. Since the required cavity size for Li^+, Mg^{2+}, and Al^{3+} are similar (based on $M^{n+}\cdots O$ bond length data[6]), it was decided to synthesize group 6 metalla-crown ether tetracarbonyl complexes, structurally similar to **1**, but with either one or two functional groups in the crown ether backbone that are capable of becoming negatively charged under appropriate circumstances. The hope was that these systems would react with appropriate organometallic derivatives to give neutral Mg^{2+} and Al^{3+} benzoylates, structural analogues to the Li^+ benzoylate complexes **2**. In this paper we describe the synthesis of the group 6 metalla-crown ether tetracarbonyl complexes **3–7** containing C(O)NH or P–NH amido groups in the crown ether backbone. In the presence of organometallic reagents (RLi, RMgCl, etc.), it was anticipated that these functional groups would deprotonate to give anionic crown ether ligand systems. The reactions of these complexes with RLi, RMgCl, "3RLi + $AlBr_3$", and $LiAlH_4$ are described.



1 A = O, NMe

R_2' = Ph_2, MeN⌒NMe

2 (R = Ph, Me)

(eq 1)

Results

The α,ω-di-P-donor ligands **9–11** required for the synthesis of **3** and **4** were prepared from the reaction of R'_2PCl with the appropriate diol precursor that had been previ-

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(1) Powell, J.; Kuksis, A.; May, C. J.; Nyburg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941.

(2) Powell, J.; Gregg, M. R.; Kuksis, A.; May, C. J.; Smith, S. J. *Organometallics*, first of three papers in this issue.

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(4) Powell, J.; Gregg, M. R.; Kuksis, A.; Meindl, P. E. *J. Am. Chem. Soc.* **1983**, *105*, 1064.

(5) Powell, J.; Kuksis, A.; May, C. J.; Meindl, P. E. *Organometallics*,

(6) (a) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271. (b) Shannon, R. D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1976**, *32*, 751 and references therein.

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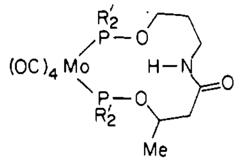
Table I. ^{1}H NMR, IR, and Elemental Analysis Data[a] for 3–11

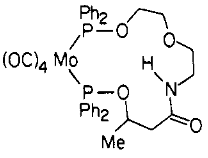
	δ(H),[b] ppm							IR data,[c] cm^{-1} (THF solutions)				
complex	CH_3	CH$_2$CH_2CH$_2$	O=CCH_2	NCH_2	OCH_2	CH	NH	ν(CO)			ν(NH)	ν(C=O)
3	1.10 (d)	1.73 (br)	2.10 (br)	3.46 (br)		4.20 (br)	6.92 (br)	2025 m	1935 s	1912 s br	3390	1676
4	1.26 (d) (NCH$_3$ 2.87 (br))	1.74 (qn)	2.33 (d)	3.29 (m)	3.67 (br)	4.30 (br)	7.61 (br)	2021 m	1908 s br	1891 s br	3390	1675
5	1.12 (d)	...	2.09 (d)	3.31 (br)		4.36 (br)	6.75 (br)	2025 m	1935 s	1912 s br	3391	1675
9[d]	1.25 (d)	1.80 (qn)	2.49 (d)	3.28 (q)	3.84 (q)	4.51 (qn)	6.85 (s)					
10	1.35 (d)	1.84 (qn)	2.45 (d)	3.33 (m)	3.77 (q)	4.48 (sx)	6.92 (br, t)					
11	1.29 (d)	...	2.41 (d)	3.21–4.1 (m)		4.45 (sx)	6.50 (br, t)					
6	2.14	1.30 (qn br)	... (CH_2NP	2.26 (br) 2.54 (br))	...	...	3.85 (m, br)	2026 m	1922 s	1885 s br		
7				2.62 (br)	3.40 (qn, br) 3.60 (s)		~3.6	2026 m	1921 s	1885 s br		
(6 – 2H$^+$ + 2Li$^+$) ~ 23								2015 m	1905 s	1887 s, 1869 s		

[a] Elemental Anal. Calcd (found) for **3**: C, 57.00 (56.81); H, 4.50 (4.47); N, 1.90 (1.95). For **4**: C, 37.87 (37.67); H, 5.48 (5.63); N, 11.63 (11.49). For **5**: C, 56.25 (56.67); H, 4.56 (4.53); N, 1.82 (1.60). For **6**: C, 58.26 (58.57); H, 5.13 (5.31); N, 5.82 (5.45). For **7**: C, 56.43 (56.75); H, 4.70 (4.92); N, 3.87 (3.61). [b] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet, qn, quintet; sx, sextet; br, broad. [c] Abbreviations: m, medium, s, strong, br, broad. [d] Recorded in DMSO-d_6.



3 (R' = Ph)

4 (R$'_2$ = MeN NMe)



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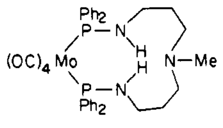

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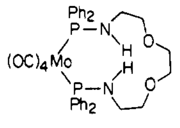
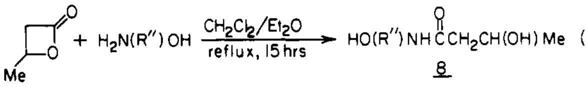


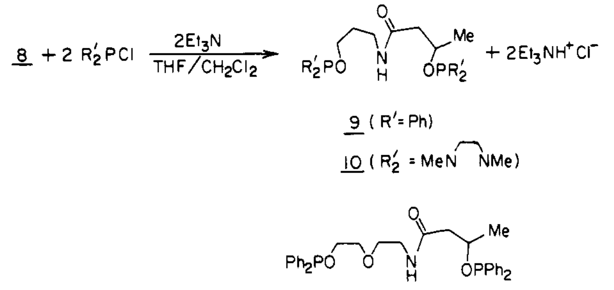
7

ously obtained from the reaction of β-butyrolactone with an amino alcohol (eq 2 and 3).[7] As compounds **9–11** were



(eq 2)

8



9 (R' = Ph)

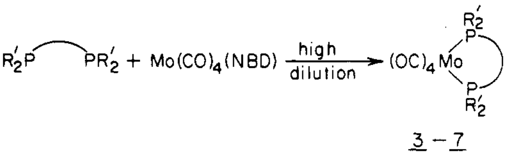
10 (R$'_2$ = MeN NMe)

11 (eq 3)

Table II. IR Data [ν(CO) Region, THF Solutions] for Benzoylate/Acylate/Formylate Complexes of the Type [Mo(CO)$_3$(RCOM)P$_2$⊃][M]$_n$ (R = Ph, Me, H; M = Li$^+$, Al^{3+})

complex	R	M	n	ν(CO), cm^{-1}		
17a	Ph	Li$^+$	1	1932	1855	1831
17b	Me	Li$^+$	1	1931	1852	1831
18a	Ph	Li$^+$	1	1923	1831	1819
18b	Me	Li$^+$	1	1922	1830	1818
19a	Ph	Li$^+$	1	1929	1845	1832
19b	Me	Li$^+$	1	1928	1843	1831
20a	Ph	Li$^+$	2	1895	1801	1705
20b	Me	Li$^+$	2	1894	1801	1707
21a	Ph	Al^{3+}	0	1933	1840 (br)	
21b[b]	Me	Al^{3+}	0	1933	1850	1820[a]
22	H	Li$^+$	2	1906	1813	1716
24a	Ph	Li$^+$	2	1903	1812	1722
24b	Me	Li$^+$	2	1902	1811	1722
25	H	Li$^+$	2	1905	1815	1725
26[c]	Me	Al^{3+}	0	1930	1840	1810[a]
28a	Ph	Li$^+$	2	1905	1815	1725
28b	Me	Li$^+$	2	1905	1815	1725
29	H	Li$^+$	2	1910	1820	1734
31a[d]	Ph	Li$^+$	0	1936	1854	1833
31b[d]	Me	Li$^+$	0	1934	1858	1832

[a] Nujol mull. [b] Elemental Anal. Calcd (found) for **21b**: C, 56.79 (56.47); H, 4.99 (5.17); N, 5.52 (5.31); Al, 3.55 (3.31). [c] Calcd (found) for **26**: C, 55.12 (54.95); H, 4.59 (4.56); N, 3.67 (3.58); Al, 3.54 (3.25). [d] Taken from ref 2.



(eq 4)

3 – 7

not easily purified, care was taken to use freshly distilled, dry reagents and the ligands **9–11** were used "as is" subject to satisfactory NMR characterization (Table I). The ligands required for the preparation of **6** and **7** were similarly prepared from Ph$_2$PCl and the appropriate α,ω-diamine. Complexes **3–7** were prepared by the reaction of the appropriate α,ω-di-P-donor ligand with Mo(CO)$_4$(norbornadiene) in CH$_2$Cl$_2$ at 20 °C using high-dilution conditions and long reaction times (ca. 4 days) (eq 4). The complexes were characterized by IR and ^{1}H and ^{31}P{^{1}H}-NMR spectroscopy and elemental analysis (Tables I and II). Besides a typical Mo(CO)$_4$ pattern, the IR spectra of **3–5** contained an amide ν(N–H) at 3390 cm^{-1} and an amide ν(CO) stretch at 1676 cm^{-1}. The reaction of **3** with

$Ph_2PN(Me)(CH_2)_3N(Me)(CH_2)_3N(Me)PPh_2$

12

$Ph_2PNHCH_2(CH_2OCH_2)_2CH_2NHPPh_2$

13

2.2 molar equiv of PhMgCl in THF resulted in the loss of the amido ν(NH) and ν(C=O) absorptions of **3** while the "Mo(CO)$_4$" absorptions were essentially unchanged. Addition of Mg(OEt)(O$_2$CCF$_3$) to **3** gave the same result consistent with deprotonation of the –NHC(O)– group to give the anionic 12C3 species **14** being the only result of the reaction of **3** with PhMgCl (eq 5). If a molar equiv-

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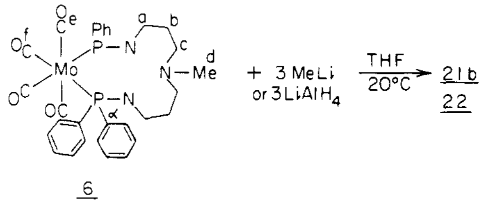
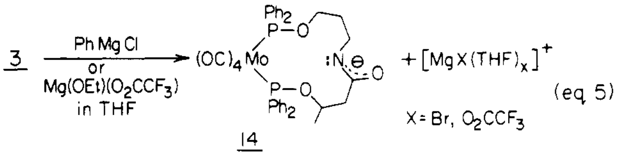
[7] Gresham, T. L.; Jansen, J. E.; Shaver, F. W.; Bankert, R. A.; Fiedorek, F. T. *J. Am. Chem. Soc.* **1951**, *73*, 3168.

Table III. $^{13}C\{^1H\}$ NMR Data Recorded in THF/CD_2Cl_2 Solution

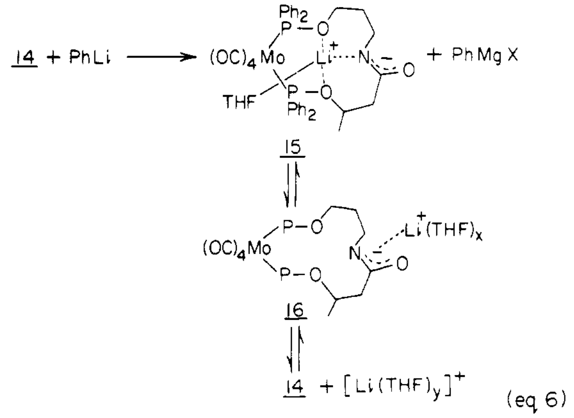


complex	δ(C), (ppm) ($^2J_{^{31}P-^{13}C}$, Hz) a	b	c	d	e[a]	f[a]	α[a]	acyl Me	acyl C=O
6	45.1	26.6	60.1	42.2	210 (10)	215 (10)	140	...	...
21b	47.9	*b*	58.1	44.5	228 (10)	227 (10)	147 149	49.0	342.8
22	48.52	24.8?[b]	57.8	45.2	231 (10)	227 (9.5)	142 145		

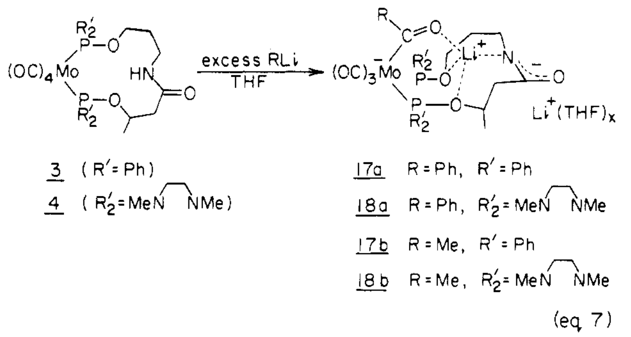
[a] 1:2:1 triplets—coupled to two equivalent ^{31}P nuclei. [b] Masked by THF resonances.



alent of PhLi was added to **14** (formed in situ, eq 5), a new ν(CO) absorption was observed at 2012 cm^{-1} (close to the 2025 cm^{-1} absorption of **14**) and the remaining ν(CO) absorptions were broadened relative to **14** alone. The relative intensity of the 2012 cm^{-1} absorption vis à vis the 2025 cm^{-1} absorption was found to be concentration dependent, being of lower intensity for more dilute solutions suggestive of an equilibrium between complexed (encapsulated) Li$^+$ species **15** and solvated Li$^+$ species **16** and **14** (eq 6).



When excess RLi is added to THF or benzene solutions of **3** or **4** on a synthetic scale, a yellow/orange precipitate rapidly formed. The IR spectrum of a dilute solution of **3**/**4** + 3 equiv of RLi in THF is consistent with these products being the "*fac*-Mo(CO)$_3$" benzoylate/acylate derivatives **17** and **18** (eq 7; Table III and Figure 1a–c).



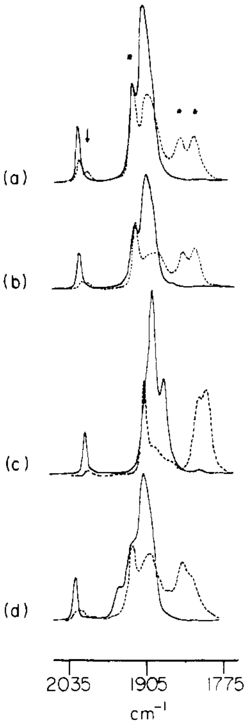
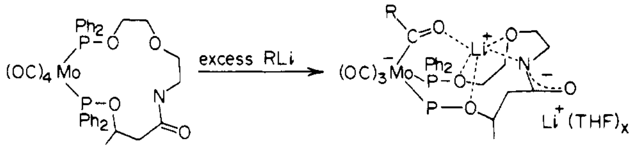


Figure 1. The IR spectra [ν(CO) region of 7.25 × 10^{-3} M THF solutions of (—) and the spectra after the addition of 3 equiv of RLi (---): (a) complex **3** (+3MeLi); (b) **3** (+3PhLi); (c) **4** (+3PhLi); (d) **5** (+3PhLi). Absorptions associated with the benzoylate/acylate products are marked with asterisks. The arrow represents the high-frequency ν(CO) absorption of the [Mo(CO)$_4$\{P$_2$⊃-H$^+$\}]Li$^+$ lithium-encapsulated species (e.g. **15**, eq 6).

Attempts to recrystallize these products from CH$_2$Cl$_2$/hexane resulted in their rapid decomposition to give the starting tetracarbonyl **3** or **4** (as does addition of MeOH to **17**). The IR data [ν(CO) region] for **17** and **18** are very similar to those of the previously reported complexes of the type **2**.[1-5] The IR spectrum of **3**, after the addition of 3 equiv of MeLi (Figure 1b), is consistent with the presence in the THF solution of a mixture of **15** ⇄ **16** ⇄ **14** (eq 6) and the acylate **17b** (eq 7). Addition of excess MeLi converts the system completely to **17b**.

Addition of PhMgCl to the 13C4 system **5** resulted in loss of the amido ν(NH) and ν(C=O) absorptions while the ν(CO) absorptions were essentially unchanged. This is consistent with deprotonation of the –NH(CO)– group *without* complexation (encapsulation) of Mg^{2+} (analogous to eq 5). Addition of RLi resulted in the formation of deprotonated species, analogous to **14**, **15**, and **16** (eq 6), and the benzoylate/acylate products **19** (eq 8; Figure 1d and Table II). At "Mo" concentrations greater than 10^{-2} M the benzoylate/acylate products **19** precipitate from THF as yellow/orange highly reactive compounds.



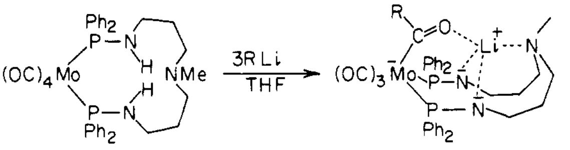
5

19a R = Ph

19b R = Me

(eq 8)

Reaction of 6 with RLi and LiAlH$_4$. The complex Mo(CO)$_4${Ph$_2$PNH(CH$_2$)$_3$NMe(CH$_2$)$_3$NHPPh$_2$} (**6**) reacts with 3 equiv of RLi (R = Ph, Me) in THF to give the benzoylate/acylate complexes **20** (eq 9). These complexes, which could be isolated as highly reactive yellow/orange powders, were characterized by IR [ν(CO) region] and ^{13}C{^{1}H} NMR (Tables II and III). Reaction of the acylate **20b** (formed in situ in THF) with AlBr$_3$ gave relatively insoluble orange crystals that were characterized as [Mo(CO)$_3$(MeCOAl){Ph$_2$PN(CH$_2$)$_3$NMe(CH$_2$)$_3$NPPh$_2$}] (**21b**) on the basis of elemental analysis and IR data (eq 10 and Table II). The corresponding benzoylate **21a** was much more soluble. Crystals of **21b** were not suitable for single-crystal X-ray diffraction studies. Addition of EtOH to a suspension of **21b** resulted in the regeneration of the tetracarbonyl **6**. Reaction of **6** with 3 equiv of LiAlH$_4$ in THF gave an orange solution, the IR spectrum of which is consistent with the formation of a "*fac*-Mo(CO)$_3$" species which is postulated to be the formylate complex **22** (eq 11 and Table II). Two equivalents of H$_2$ gas were evolved in this reaction, and no CO or CH$_4$ was detected (IR monitoring). Repeated attempts to isolate **22** from solution were not successful. Nor could a complex structurally analogous to **21** be obtained from the reaction of **22** with AlBr$_3$ although the IR spectrum of these solutions contained ν(CO) absorptions at 1934, 1853, and 1824 cm^{-1} very close to those observed for **21**. Reaction of **6** with excess LiBHEt$_3$ or with 2 equiv of LiAlH$_4$ resulted in deprotonation only to give [Mo(CO)$_4${Ph$_2$PN(CH$_2$)$_3$NMe(CH$_2$)$_3$NPPh$_2$]Li$_2$ (**23**, formed in situ; IR data given in Table I). The ^{13}C{^{1}H} NMR spectrum of the formylate **22** is very similar to that of the acylate **20b** (Table III). However attempts to locate a resonance associated with the formylate carbon were not successful (see comments in the Discussion). When solutions of **22** (in situ with AlH$_3$ in THF) were refluxed for 4 h, a hydride signal at δ −5.5 ppm (1:2:1 triplet; $^2J_{^{31}P-^1H}$ = 14 Hz; THF-d_8 solution) was observed in the ^{1}H NMR consistent with formation of [Mo(CO)$_3$H{Ph$_2$PN(CH$_2$)$_3$NMe(CH$_2$)$_3$NPPh$_2$}]$^{3-}$3Li$^+$ (approximately 40% based on the integration of hydride to ligand proton resonances).

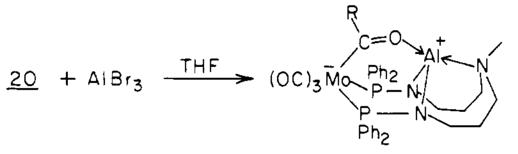


6

20a R = Ph

20b R = Me

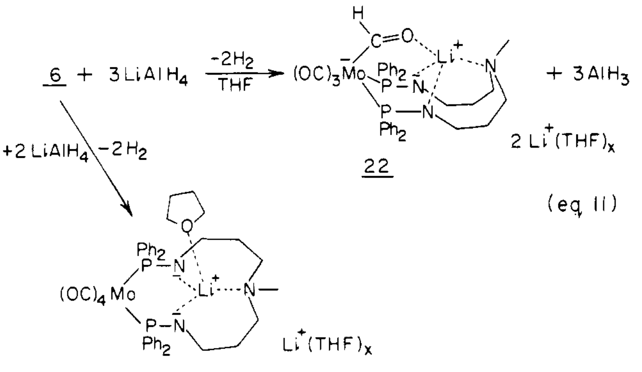
(eq 9)



21a R = Ph

21b R = Me

(eq 10)

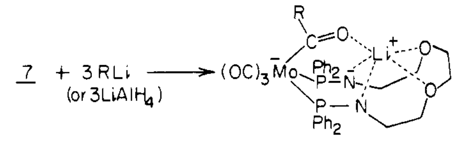


22

23

(eq 11)

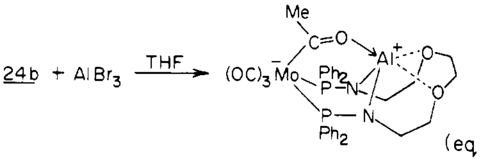
On the basis of IR studies (Table II) the aza-13C4 complex **7** reacts with RLi and LiAlH$_4$ to give *fac*-[Mo(CO)$_3$(RCOLi){Ph$_2$PNCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$NPPh$_2$}]$^{2-}$Li$^+_2$ [R = Ph (**24a**), Me (**24b**), H (**25**) (eq 12)]. Addition of AlBr$_3$ to THF solutions of **24b** gave **26** as an orange crystalline product isolated in low yield (eq 13 and Table II).



24 R = Ph, Me

25 R = H

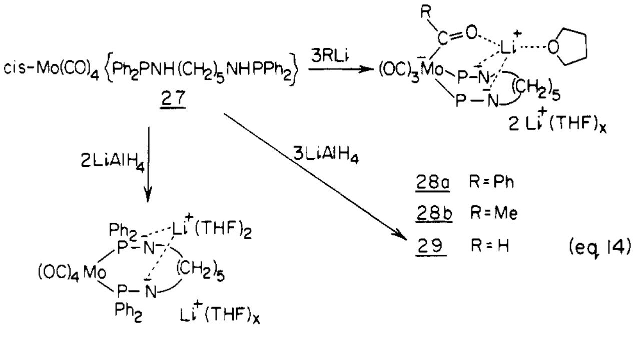
(eq 12)



26

(eq 13)

The complex Mo(CO)$_4${Ph$_2$PNH(CH$_2$)$_5$NHPPh$_2$} (**27**), synthesized for comparative purposes, was also found to react with RLi and LiAlH$_4$ in a similar fashion to **6** and **7** (eq 14).



27

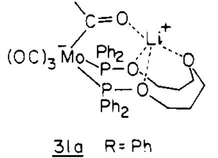
28a R = Ph

28b R = Me

29 R = H

30

(eq 14)



31a R = Ph

31b R = Me

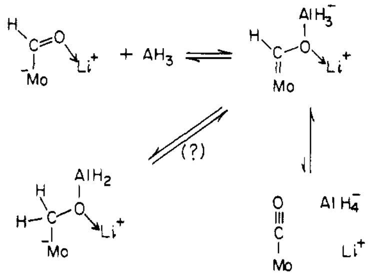
Discussion

The aim of this work was the synthesis of suitably functionalized ditopic ligands which, when complexed to give *cis*-Mo(CO)$_4$P$_2\supset$, would result in complexes that would "activate" a coordinated CO to alkyl/aryl carbanion addition in the presence of Mg^{2+} or Al^{3+} cations. The metalla-aza-crown ether complexes **3**–**5**, which contain an amido group in the crown ether backbone, react with RMgCl or Mg(OEt)(O$_2$CCF$_3$) in THF to give the deprotonated amidate (e.g. **14**, eq 5). Since the ν(CO) stretches of the deprotonated complex **14** are essentially unchanged from those of the neutral tetracarbonyl **3**, it is reasonable to assume that the Mg^{2+} cation is not coordinated by the P–O oxygens. In contrast when Li$^+$ ions are introduced into a solution containing **14**, new ν(CO) absorptions at slightly lower frequency are observed consistent with some PO···Li$^+$ interaction (**15**) and the solution equilibria **15** $\rightleftharpoons$ **16** $\rightleftharpoons$ **14** (eq 6). While a shift to lower frequency (**15** vs **16**/**14**) is not consistent with simple bonding ideas, similar decreases have been observed when *cis*-Mo(CO)$_4${P(OR)(1,2-O$_2$C$_6$H$_4$)}$_2$ complexes react with RLi to form 1:1 adducts.[5] The possibility of a Li$^+$···OC interaction in **15** similar to that observed in alkali-metal salts of carbonylate anions[8] seems unlikely in that all the ν(CO)'s are moved to lower frequency while M(CO)$_x^-$···Li$^+$/Na$^+$ interactions result in shifts to both higher and lower frequencies.

The reaction of **3**, **4**, and **5** with excess RLi results in the formation of lithium benzoylate/acylates **17**–**19**. These complexes are obtained because of the additional stabilization provided by preferential Li$^+$ binding in the product. Study of molecular models allows the conclusion that N···Li$^+$ (rather than O···Li$^+$) coordination of the amidate group and this gives rise to an *aza*-12C3 structure similar to the previously reported systems **31**.[2,5] While structurally analogous to the neutral complexes **2** (eq 1) and **31**, complexes **17**–**19** are much more readily converted back to the starting tetracarbonyl complex. This is probably a consequence of the ease with which the amidate group is protonated with resultant loss of Li$^+$ binding. A comparison of the IR spectra for the reaction of **3**, **4**, and **5** with 3 molar equiv of PhLi (Figure 1a,c,d) shows that the benzoylate is present in a greater amount for the "MeNCH$_2$CH$_2$N(Me)P" system (Figure 1c) consistent with previous observations on the effect of phosphorus substituents on the basicity of PO oxygens and benzoylate stability.[5] These results suggest that Li$^+$ binding is more effective than Mg^{2+} binding for the stabilization of the benzoylate/acylate products.

The complex Mo(CO)$_4${Ph$_2$PNH(CH$_2$)$_3$NMe(CH$_2$)$_3$NHPPh$_2$} (**6**) was synthesized with a view to obtaining neutral benzoylate/acylate complexes in which Al^{3+} is selectively bonded. Reaction of **6** with 2 molar equiv of LiAlH$_4$ result in the smooth deprotonation of **6** to give the anionic tetracarbonyl complex **23**. (Reaction of **6** with 2RLi gave mixtures of **6**, **23**, and **20**). The shift to lower frequencies for the CO's of **23** relative to **6** (2015, 1905, 1887, and 1869 cm^{-1} vs 2026, 1921, and 1885 cm^{-1}, respectively) is consistent with Li$^+$ complexation as shown (eq 11). The deprotonated complex **23** is structurally similar to the previously reported species *cis*-Mo(CO)$_4${Ph$_2$NLi}$_2$.[9] When **6** (7 × 10^{-3} in THF) is reacted with 3 equiv of RLi, the system is completely converted to the benzoylate/acylate **20** in comparison to "**3**–**5** + 2RLi" which are only partially converted under these conditions (Figure 1). It seems likely that the triply negatively charged anion in **20** more strongly binds the Li$^+$ cation vis à vis the doubly negative anion in **17**–**19**. The fact that the complex Mo(CO)$_4${Ph$_2$PNH(CH$_2$)$_5$NHPPh$_2$} (**27**) reacts with 3RLi to give the benzoylate/acylates **28** supports this hypothesis and illustrates that total encapsulation of Li$^+$ is not a prerequisite for CO activation in these systems. Reaction of **20** with AlBr$_3$ gives the neutral complexes **21** which contain encapsulated Al. The IR absorptions [ν(CO) region], of **21** are very similar to those of **2** and **31** (see Table II) and ca. 50 cm^{-1} to higher frequency than those of **20**. This suggests strong, covalent PN–Al bonds. The insolubility of the acylate **21b** suggests probable intermolecular binding in the crystal and the possibility of a five-coordinate Al. The postulated structure **21** is similar to the dimethylamidate derivative [Fe(CO)$_4$(Me$_2$NCO)Al(NMe$_2$)$_2$]$_2$ which is thought to contain four-coordinate tetrahedral "AlN$_3$O" units.[10]

Scheme I



The reaction of **6** with 3 equiv of LiAlH$_4$ in THF proceeds smoothly to give the *postulated* formylate complex **22** (eq 11). The formulation of **22**, which we have as yet been unable to isolate in crystalline form, is based on the following observations: (i) In the formation of **22** (eq 11) 2 molar equiv of H$_2$ are evolved; (ii) no CO is evolved; (iii) conversion from a "Mo(CO)$_4$" to a "Mo(CO)$_3$" system occurs on addition of the third equivalent of LiAlH$_4$ (no reaction is observed between **6** and AlH$_3$); (iv) on refluxing THF solutions of **22** (with in situ AlH$_3$) a hydridic species slowly forms consistent with loss of CO from a formylate;[11] (v) the possibility of a reductive loss of CO with coordination of the ligand NMe group to the molybdenum can be excluded on the grounds that neither prolonged refluxing of **6** in THF nor photochemical irradiation of **6** result in CO loss;[12] and (vi) the IR [ν(CO) region], and ^{13}C{^{1}H} NMR spectra are very similar to those of the benzoylate/acylate **20**. The lack of a formylate carbon resonance in the ^{13}C{^{1}H} NMR spectrum of **22** may be a consequence of solution exchange processes in the relatively concentrated NMR sample solution of **22** (prepared in situ from **6** + 3LiAlH$_4$). One possibility is illustrated in Scheme I. An alternative explanation is that the major solution species contains a "MoCH$_2$OAl(Li)" unit as illustrated by **32** (Scheme I). While the data do not as yet fully delineate the *exact* nature of **22**, it is clear that preferential Li$^+$ binding by the use of a ditopic ligand system has the ability to provide additional stability to a formylate ligand and hence promote addition of a hydride to a coordinated CO. Although studied in less detail, complex **7** reacts with LiAlH$_4$ in an analogous manner to that of **6**.

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[12] Kyba and Brown have previously reported that displacement of a CO from "M(CO)$_4$P$_2\supset$" systems is ligand assisted and that in sterically constrained "PNP" systems CO loss to give "M(CO)$_3$PNP" does not occur even under very vigorous conditions. Kyba, E. P.; Brown, S. B. *Inorg. Chem.* **1980**, *19*, 2159.

On the basis of the relative amounts of benzoylate/acylate formation upon the addition of RLi to 7 × 10^{-3} M "$Mo(CO)_4P_2$" complexes in THF (20 °C), a qualitative order of benzoylate/acylate stability is **20**, **24** ≥ **28** > **18** > **17** ~ **19** > $[Mo(CO)_3(RCOLi)(Ph_2PO)_2]Li$ (formed from the reaction of *cis*-$[Mo(CO)_4\{(Ph_2PO)_2H]Et_3NH$[9] with 3 equiv of RLi). The ease of hydride addition ($LiAlH_4$) to CO in $Mo(CO)_4P_2$ systems decreases in the sequence **6** > **2** (A = NMe) > **2** (A = O) (does not react with $LiAlH_4$[2]). Efforts to further characterize the *postulated* formylate systems **22**, **25**, and **29**, and ligand modifications aimed at further "stabilizing" formylate systems through "cooperativity" effects are in progress.

Experimental Section

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on one of the following instruments: Varian T-60, CFT-20, or XL-200 spectrometer. Infrared spectra were recorded on Nicolet 5DX, 10DX, and 7000 series Fourier Transform infrared spectrometers using 0.5-mm NaCl solution cells. Elemental analyses were done by Canadian Microanalytical Laboratories, Vancouver, British Columbia, Canada.

All reactions were carried out under a nitrogen atmosphere. Dichloromethane was distilled from P_2O_5; pyridine was distilled over KOH; triethylamine (Et_3N) was distilled over $LiAlH_4$; diethyl ether, tetrahydrofuran (THF), and benzene were distilled from sodium benzophenone ketyl. Diphenylchlorophosphine was purchased from the Aldrich Chemical Co. and distilled (reduced pressure) prior to use. $Me\overline{NCH_2CH_2N(Me)P}Cl$ was prepared from the reaction of *N*,*N'*-dimethyl-1,2-diaminoethane with PCl_3 in benzene at 5 °C in the presence of 2 molar equiv of Et_3N and distilled prior to use. (Considerable care should be taken in handling this compound.[13]) Phenyllithium, methyllithium, and phenylmagnesium chloride solutions were purchased from the Aldrich Chemical Co. and standardized with diphenylacetic acid prior to use. $Mg(OEt)(O_2CCF_3)$ was prepared in situ by the addition of a molar equivalent of CF_3CO_2H to a suspension of $Mg(OEt)_2$ in THF. β-Butyrolactone, 3-propanolamine, 2-(2-hydroxyethoxy)ethylamine, triethylene glycol, *N*,*N'*-dimethyl-1,2-diaminoethane, and 3,3'-diamino-*N*-methyldipropylamine were purchased from the Aldrich Chemical Co. Reagents were dried and distilled under reduced pressure prior to use. $Mo(CO)_4$(norbornadiene) was prepared by a published procedure.[14] *N*-(3-Hydroxypropyl)-β-hydroxybutyramide and *N*-[(2-hydroxyethoxy)-2-ethyl]-β-hydroxybutyramide were prepared from the reaction of β-butyrolactone with propanolamine or 2-(2-hydroxyethoxy)ethylamine in refluxing 60:40 CH_2Cl_2/Et_2O.[7] Removal of the solvent gave the required compounds as viscous oils that were used without further purification. The Gabriel synthesis[15] was used to prepare 3,6-dioxa-1,8-octanediamine from 3,6-dioxa-1,8-octane dichloride (purchased from Aldrich).

α,ω-Di-P-donor ligands were prepared are outlined in eq 3. A typical procedure is illustrated for the synthesis of ***N*-{3-[(diphenylphosphino)oxy]propyl}-β-[(diphenylphosphino)-oxy]butyramide (9)**. To a solution of 11.78 g (0.074 mol) of *N*-(3-hydroxypropyl)-β-hydroxybutyramide and 20.6 mL of Et_3N (0.15 mol) in 300 mL of THF was slowly added 32.5 g (0.15 mol) of Ph_2PCl. After being stirred for 1 h, the mixture was filtered, to remove $[Et_3NH]Cl$, and evaporated to dryness to give **9** as a viscous oil, >90% yield. The oil was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. If the spectrum integration was not close to that expected, the oil was not used in subsequent reactions and the synthesis repeated.

The metalla-crown ether complexes 3–7 were prepared as outlined in eq 4. A typical reaction is illustrated for the synthesis of **$Mo(CO)_4\{Ph_2PO(CH_2)_3NHC(O)CH_2CH(Me)OPPh_2\}$ (3)**. A solution of 9.66 g of $Mo(CO)_4(NBD)$ was dissolved in 250 mL of dry CH_2Cl_2 and loaded into a 250-mL Marriotte-type pressure-equalizing constant addition funnel. Exactly 1 equiv of **9** (22.60 g) was dissolved in 250 mL of dry CH_2Cl_2 and placed in a second Marriotte-type pressure-equalizing constant addition funnel. The two solutions were then added simultaneously and dropwise to 3500 mL of dry CH_2Cl_2 over a period of 15–20 h. The whole apparatus was shielded from light as much as possible. The mixture was stirred for a further 72 h at 20 °C. The solvent was then concentrated to 50 mL on a rotary evaporator. Approximately 100 mL of acid-washed cellulose powder was then stirred into the concentrated reaction mixture. The solvent was removed by a rotary evaporator. The "cellulose powder/reaction residue" was dried in vacuo and added to the top of a 30-mm diameter column packed with glass wool, sand, a 60-cm column length of "Florisil" (magnesium silicate), and more sand (bottom to top description of column packing) filled with hexanes. The column was eluted with ca. 1 L of ACS hexanes, 2 L of 1:1 hexanes/CH_2Cl_2, and 2 L of CH_2Cl_2 and then stripped by using 500 mL of acetone. The hexane/CH_2Cl_2 and CH_2Cl_2 fractions were combined and reduced to 250 mL by rotary evaporator. A further 150 mL of hexanes was added and the solution reduced to 50 mL during which time complex **3** precipitated as a white crystalline solid (isolated yield 62%). The following complexes were similarly prepared: **4** (32%); **5** (40%); **6** (60%); and **7** (40%).

Synthesis of $Mo(CO)_3(MeCOAl)\{Ph_2PN(CH_2)_3NMe(CH_2)_3NPPh_2\}$ (21b). To a solution of 0.216 g of **6** in 15 mL of THF was added 0.69 mL of 1.3 M methyllithium in Et_2O. After 5 min 0.080 g of anhydrous $AlBr_3$ was added and the resultant solution allowed to stand for 5 h. The resultant orange powder was filtered and washed with THF to give 0.057 g of **21b** (25% yield). Complex **24b** was similarly isolated in 8% yield. When stirred with 3 equiv of ethanol in THF, complex **21b** slowly reacts and goes into solution. The IR spectrum after 20 min is consistent with the regeneration of the $Mo(CO)_4P_2$ complex **6**.

Reaction of $Mo(CO)_4\{Ph_2PNH(CH_2)_3NMe(CH_2)_3NHPPh_2\}$ (6) with $3LiAlH_4$. To a solution of 0.721 g of **6** in 15 mL of THF was added 0.114 g of $LiAlH_4$ (3 equiv), and the solution was stirred for 1 h at 20 °C. A total of 49 mL of gas (≈2 equiv) were evolved. The gas was identified as hydrogen (gas chromatography and mass spectrometry). The volume of the solution was evaporated to dryness, and 1.0 mL of THF-d_8 and 1.0 mL of CD_2Cl_2 were added. This solution was used to monitor the ^1H and $^{13}C\{^1H\}$ NMR spectra. Strong absorptions associated with THF masked parts of the spectra.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for financial support.

Registry No. **3**, 84558-21-4; **4**, 123239-08-7; **5**, 123239-09-8; **6**, 84537-77-9; **7**, 123239-10-1; **8** (R'' = *n*-propyl), 123207-78-3; **9**, 123207-79-4; **10**, 123207-80-7; **11**, 123207-81-8; **12**, 123207-82-9; **13**, 123207-83-0; **14** (MgBr), 123263-82-1; **14** (MgO_2CCF_3), 123239-31-6; **17a**, 123239-23-6; **17b**, 123239-24-7; **18a**, 123239-25-8; **18b**, 123239-26-9; **19a**, 123239-27-0; **19b**, 123239-28-1; **20a**, 123239-11-2; **20b**, 123239-12-3; **21a**, 123239-13-4; **21b**, 84537-78-0; **22**, 123239-14-5; **23**, 123239-21-4; **24a**, 123263-80-9; **24b**, 123239-15-6; **25**, 123239-16-7; **26**, 123239-17-8; **27**, 123239-22-5; **28a**, 123239-18-9; **28b**, 123239-19-0; **29**, 123239-20-3; Ph_2PCl, 1079-66-9; $Mo(CO)_4(NBD)$, 12109-74-9; PhMgCl, 100-59-4; $Mg(OEt)(O_2CCF_3)$, 123207-84-1; $[Mo(CO)_3H\{Ph_2PN(CH_2)_3NMe(CH_2)_3NPPh_2\}]Li_3$, 123263-81-0.

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